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Assessing Volatile Fatty Acids production from food waste at MBT plants: focusing on temperature influence

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SUMMARY

The implementation of the circular economy paradigm requires a change in economic dynamics towards more sustainable and renewable strategies. Under this scenario, waste is not considered a residue but instead a source of add-value products.

The Organic Fraction of Municipal Solid Waste (OFMSW) represents around the 30% of the municipal solid waste and its treatment is a big challenge to deal with since the European union restricted its landfilling. Thermal treatment such as incineration and pyrolysis have high energy requirements and greenhouse gas emissions (GHG) while biological treatments, such as composting and anaerobic digestion (AD), operation cost is lower but generate products (compost and biogas) with low market value.

Mechanical-Biological Treatment plants (MBT) incorporate biological stages that reduce and stabilize the biodegradable matter present in the OFMSW. The AD process can be engineered to promote the accumulation of fermentation products such as Volatile Fatty Acids (VFA) including acetic, propionic and butyric acid, among others. VFA have a higher market price than biogas and have a wide range of utilities. However, there is still some controversy regarding the impact of operational conditions on VFA yield and VFA profile. Therefore, this research investigates the influence of temperature as operational parameter to maximize VFA production from OFMSW and minimize methanogenic activity at different temperatures.

Experimental results have shown that the configuration of MBT plant using wet AD with supernatant from AD recirculation is ideal for VFA production since the waste liquid stream under treatment has high alkalinity, a pH near 6 and readily organic matter available to be fermented into VFA. Fermentation under mesophilic conditions (35 ^{o}C) have been increased VFA concentration from 6 g VFA/L to 20 g VFA/L which is in the top-tier of values in the literature. Experiments at different temperatures (20, 45, 55 and 70 ^{o}C) have shown that both the ratio COD_{VFA}/sCOD and specific production ($gCOD_{VFA}$/gVS) decreased as temperature increased even that the differences at 45 and 55 ^{o}C from 35 ^{o}C were slight. Nevertheless, 20 ^{o}C resulted to be an unfeasible temperature for VFAs production. This investigation could generate an alternative for biorefinery innovations and valorization of OFMSW.

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NOMENCLATURE

AD: Anaerobic Digestion
COD: Chemical Oxygen Demand
COD_{VFA}: Chemical Oxygen Demand due to volatile fatty acids
csCOD: complex soluble Chemical Oxygen Demand
FW: Food Waste
GHG: Greenhouse gases
HRT: Hydraulic Retention Time
MBT: Mechanical-Biological Treatment plant
OFMSW: Organic Fraction from Municipal Solid Waste
OLR: Organic Loading Rate
PHA: Polyhydroxyalkanoates
sCOD: soluble Chemical Oxygen Demand
tCOD: total Chemical Oxygen Demand
TS: Total Solids
VFA: Volatile Fatty Acids
VS: Volatile Solids

1. INTRODUCTION

The current economic dynamics requires more sustainable and renewable strategies to maximize recovery from residual flows, enhancing the importance of circular economy. Worldwide, OFMSW is the most produced fraction of MSW, being an opportunity to recover useful products, such as bio-energy and/or compost [1]. The OFMSW from MBT plant is typically used to produce biogas and compost as final products, which have a lower market price in comparison with other add-value compounds that can also be produced such as volatile fatty acids (VFA). VFA, can be used as precursors of fertilizers, biodiesel, or bioplastics, among others. The situation of food waste (FW) and the role of MBT plants in the management of the OFMSW, as well as the implementation of alternative valuable products production, is described in the sections below.

1.1. FOOD WASTE

One-third of food produced for human consumption is lost or wasted, which amounts to about 1.3 billion tons per year worldwide representing a waste of resources used in production such as land, water, energy and inputs, increasing greenhouse gases (GHG) emissions in vain [2]. Food Waste (FW) is basically composed by organic matter (e.g., polysaccharides, proteins and lipid) rich streams. While treatments such as incineration or pyrolysis, involves high energy demand for organic municipal waste due to the high humidity of this material, anaerobic digestion is considered as a reliable biological treatment process due the high energy recovery and its limited environmental impact [1].

According to *Agència Catalana de Residus* (ACR), over 3,161,812 people living in Barcelona Metropolitan Area is producing an average of 1.42 kg of waste per day. In Catalonia, almost the 30% in weight corresponds to organic matter [3] that should be disposed into the organic selective container. Nonetheless, recycling awareness is still emerging and other materials such as glass, plastics and other impurities are present in the waste. Thus, it is needed to apply mechanical pre-treatments before treating the organic material through biological systems.

1.2. MECHANICAL-BIOLOGICAL TREATMENT PLANT (MBT)

Organic waste is the center of many environmental problems such as greenhouse gas emissions and leachate production associated with the biodegradation within landfills [4]. After European landfilling restriction (Directive 1999/31/EC), on the new waste management hierarchy landfilling is the least preferable option.

MBT plants are specialized plants in the selection and recovery of organic and refuse waste that are generated in households, commerce and small industry [5]. MBT plants consist of pre-processing stages, followed by biological stages that reduce and stabilize the biodegradable matter under controlled anaerobic and/or aerobic conditions [6]. Organic matter reduction (usually expressed as Volatile Solids (VS) content) is requested since is related with lower GHG emissions, leachate pollutants and disposal weight cost [7].

The MBT plant is typically divided in the following steps: reception, selection, conditioning of the organic matter, biological stabilization, and products treatment [8]. Along the process, recovery of materials is achieved for their subsequent recycling or re-use, the organic waste volume is reduced and stabilized for disposal and energy is recovered when AD is present. Although, as all processes, one fraction will not be recoverable and will be compacted and transported to landfills. In accordance with Malinauskaite *et al.* [5], the main benefits of MBT plants are:

- Recovery of add-value products: compost (organic fertilizer), bio-stabilized organic matter (spoiled land restorer), biogas (energy), plastics, metals and refuse-derived fuel to incineration.
- Maximize waste recovery and appropriate treatment.
- Reducing waste landfilling and incineration.
- Recycling of materials.

However, there is a waste fraction that will not be recoverable and will be compacted to be transported to landfills.

1.3. ANAEROBIC DIGESTION ON MBT

On MBT plants, AD is a reliable biological process to convert organic materials in renewable methane energy. AD is a chain of biological processes by which microorganisms degrade the biodegradable material in absence of oxygen in four main phases: hydrolysis, acidogenesis, acetogenesis and methanogenesis that produces mainly biogas (CH_4 + CO_2), water and a solid phase (digestate) as final products. Furthermore, other reasons such as waste volume reduction, nutrient recovery or lower GHG emissions have to be taken into account. Anaerobic degradation of organic matter requires the concerted action of a highly varied microbial population, consisting of several groups of strict and facultative bacteria strains. Previously explained, biodegradable matter is an opportunity in order to reduce fossil fuel consumption [4]. The production of methane as renewable energy makes anaerobic digestion suitable to treat organic waste streams [9].

The acidogenic fermentation produces VFA (main AD intermediate product) and other low molecular weight organic compounds of interest, such as alcohols or lactic acid. VFAs, also referred to as short-chain fatty acids (SCFAs) are fatty acids with less than six carbon atoms, there are different types and an extended variety of applications. Acid speciation will depend on diverse factors such as substrate, operational conditions (temperature, pH, ammonium content, alkalinity, retention time) or microbial consortium [10]. Acetic acid, propionic acid and butyric acid are mainly produced from biowaste streams [11]. Figure 1 illustrates that VFA have a higher market price compared with methane and include different field applications including bioplastics production, biofuels or biological nutrient removal [12].

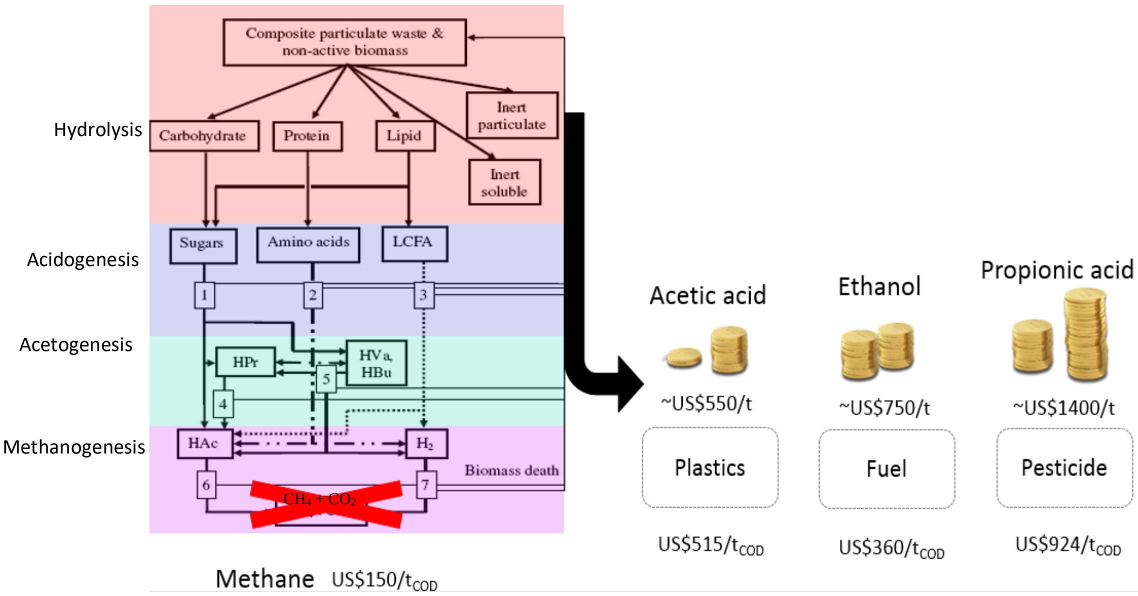

Figure 1. Anaerobic digestion scheme and VFA/methane market price (Adapted from Astals *et al.* [13]).

In acidogenic environment, hydrolytic bacteria break down complex molecules forming simple monomers that acidogenic bacteria use to the formation of H_2, CO_2, VFA or pyruvate, the latter, precursor of VFA that can be converted into acetic acid through acetogenic bacteria [14].

Acidogenic bacteria promote the formation of acetic acid (C2), propionic acid (C3), butyric acid (C4) and valeric acid (C5). The higher chain fatty acids (C3 and above) are further oxidized to acetic acid by VFA oxidation through the action of syntrophic bacteria (H_2-producing acetogenic bacteria). As is underlined in Figure 1, the boosted VFA production would lend an economically viable bio-process since are high profitable add-value products [15]. In the following overview (Figure 2), the metabolic pathways explained before are shown.

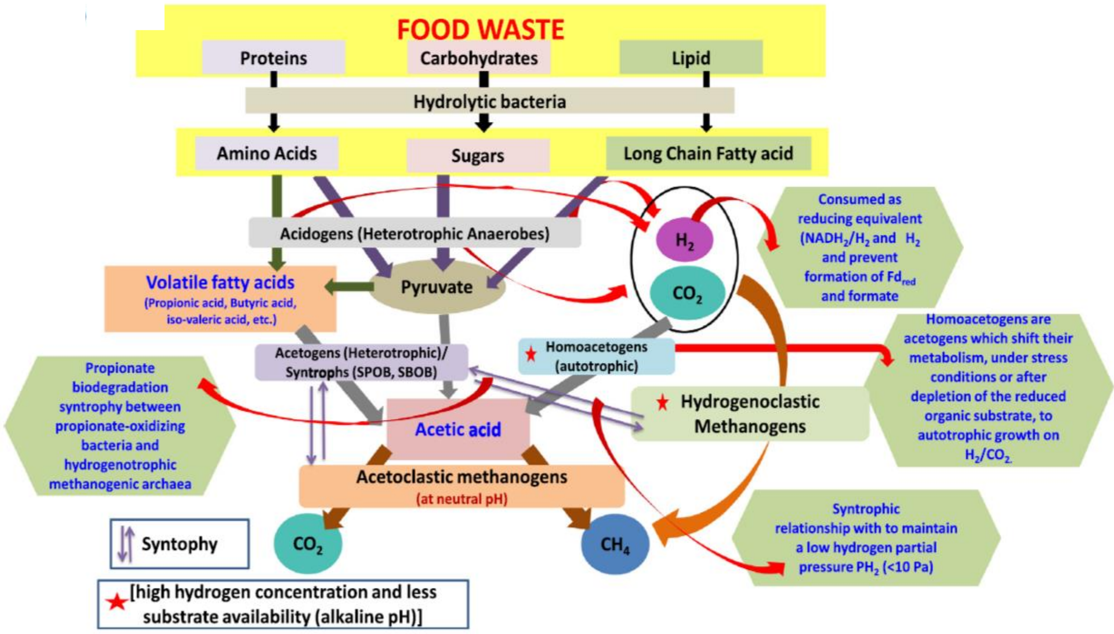

Figure 2. Metabolic Role of microorganisms for acidogenic fermentation of food waste (Dahiya *et al.* [15]).

The interest to avoid methanogens is needed to increase the concentration of these intermediate products, since the conversion of acetate into methane. Methanogens are sensible to several parameters such as pH, temperature, VFA accumulation, NH_3, heavy metals, etc [13]. The initial conditions parameters on MBT waste resulted to accomplish and favor VFA production, suggesting the improvement of the acidogenesis phase since it already inhibits partially methanogens activity.

1.3.1. TEMPERATURE INFLUENCE ON VFA PRODUCTION

Organic residues are characterized to be particulate organic matter which present limited hydrolysis step, restricting the degradation into simple molecules and future conversion into VFA. Several pre-treatments have been employed e.g. biological, chemical, mechanical or thermal, to improve hydrolysis bacteria activity and gain accessible biodegradable organic matter. Moreover, temperature affects the fermentation and methanogenesis phases. Improving VFA production from FW, chemical and thermal pre-treatments and their combination are the preferred methods [14]. Pre-fermentation induced along the plant process resulted to be an economically favorable way for VFA production as this extra time can aid the solubilization of more complex substrates to be used by fermenters microorganisms.

It has been reported that temperature is an important operational factor to improve VFA production since it affects the enzyme activity, growth of microorganisms, and hydrolysis rate [16]. Many authors have reported VFA production at different temperatures from OFMSW [17,18] or FW [19]. From psychrophilic (T < 25 ^{o}C) to mesophilic (T = 25 - 45 ^{o}C) and thermophilic (T > 45 ^{o}C) different results were obtained due to the established temperature condition since each microorganisms group have an optimum growth temperature. Temperature is a key parameter in acidogenic fermentation, since a change of operational temperature could enhance metabolism activity. Hence, promote the production of specific fermentation products.

Several acidogens microorganisms cannot survive at hyperthermophilic temperatures (> 60 ^{o}C) surpassing acidogenic bacteria optimal growing temperature [20]. Nevertheless, 20 ^{o}C is not considered as a suitable operational temperature since VFA production can be notably diminished due to low hydrolysis rate. Nevertheless, hyperthermophilic temperatures are interesting since it assumes an effective pathogen removal on the final product providing higher organic matter sanitation for subsequent applications as agricultural uses.

1.3.4. VOLATILE FATTY ACIDS CONCENTRATION AND EXTRACTION

The price of a product is fundamental for the viability of a process. The separation from the reaction medium and boosting the production of VFA are the challenges to overcome [21]. From an industrial point of view, it is convenient to evaluate the uses of producing VFAs instead of biogas.

The main carboxylic acids obtained are propionic acid, butyric acid, valeric acid, acetic acid and lactic acid depending on the substrate employed and the operational conditions applied. From these VFA, the deprotonation of the carboxyl group gives a carboxylate anion which can be converted into salts. These salts from the carboxylates, can easily be obtained and have many applications such as feed additives or additives in the formulation of cosmetics [22]. In addition, medium chain carboxylic acids can be used in paints, resins and feeds while long chain carboxylic acids can be transformed into biodiesel, lubricants, etc. Moreover, this type of fatty acids are precursors of the polyhydroxyalkanoates (PHA) used in the polymer industry. The PHA is used mainly in packaging, to produce plastic films, disposable items, etc. and nowadays its being a top research topic for VFA applications [23, 24].

Concerning VFA extraction, liquid-liquid extraction is the better-known extraction technique which is being criticized because of its economic costs of solvents and environmental impact. Membrane approaches as electro-dialysis has been considered but is still a high cost separation method linked to membrane fouling [10]. Even techniques such as adsorption or ion exchange are being studied but there are still many trials on real effluents to determine a definitive option.

1.4. STUDY CASE

MBT plant configuration will be evaluated since it seems to generate a waste with high VFA production potential simply by leaving it in a controlled deposit in semi-anaerobic conditions. One reason to be assessed is that wet anaerobic digestion with supernatant from anaerobic digestion recirculation could increase enough the sCOD and add alkalinity which stabilize the pH, giving the option to perform a fermentation, that could allow a simpler and cheaper way than fermentation performance expenses (biomass, nutrients, agitation, pH adjustment…) and recover a considerable amount of VFA.

The OFMSW have a relatively low alkalinity and it is interesting that acidogenic fermentation carried out at uncontrolled pH seems to be enriched in acetate, butyrate, propionate, and valerate [19, 15]. Described above, anaerobic digestion supernatant from MSW is characterized by high alkalinity that would favor the fermentation, but also by high nutrient content. On the other hand, leachates from OFMSW that are rich in easily biodegradable organic matter and low in nitrogen content could lead to a high increase in the production of VFA, but originating an excessive decrease in the alkalinity of the system. The different process implemented on a MBT plant will be described and characterized below to understand the organic matter fate and assess the potential of this waste material for VFA production at different temperatures.

2. OBJECTIVES

Considering the benefits that could bring acidogenic fermentation, not just in waste management, even in order to produce valuable products as VFA, this project is focused in the following objectives:

- To evaluate the different streams characteristics from MBT plant and its influence on organic fraction waste fermentation.
- To determine if there is reproducibility during five months on VFA production and its speciation of acidogenic fermentation from MBT waste.
- To stablish the best temperature condition in order to raise VFA production from MBT waste acidogenic fermentation.

3. MATERIAL AND METHODS

3.1 . SAMPLING AND STUDY CASE

The sampling of OFMSW was carried out in a MBT plant of Barcelona. Waste samples were mixed, homogenized and directly collected from the plant into plastic containers of 0.5L or 1L. Soluble fraction of the samples were obtained filtering the samples once at the laboratory by centrifugation (10,000 RPM and 20 min) and filtration (0,45 µm). All samples and subsamples were preserved at 4 ^{o}C until analysis.

The MBT plant under study treats 240,000 t/year (mix of 170,000 t/year of refuse waste and 70,000 t/year of organic waste) recovering methane from the selective organic waste that supposes the number of 13 GWh annually as energy for the plant. A processes diagram is shown on Figure 3 in order to study each unity function and influence on the organic waste. Moreover, are included the five streams points that were characterized while the project period: Leachate of OFMSW (1), Pulper output (2), Digester input (3), Digester output (4), and Liquid phase recirculation (5).

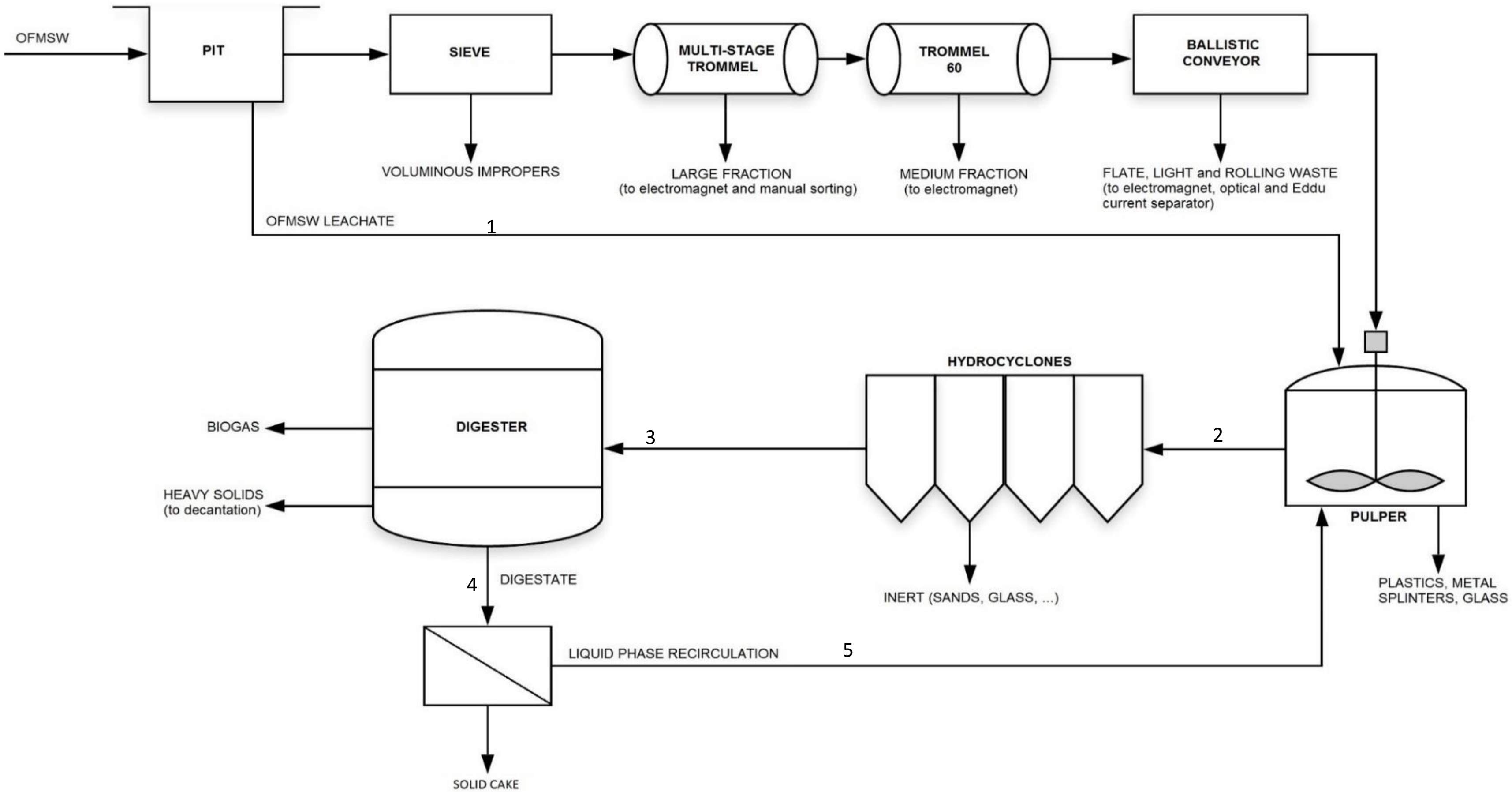

Figure 3. MBT plant process diagram.

Next, the different processes that include the plant will be briefly described:

- **Pit:** Once the waste is weighed, is stored until the treatment begins. The stored time can be important due to waste possible degradation and associated leachate production.
- **Sieve:** After the waste is grabbed from the pits, the dry mechanical pre-treatment is started separating the larger waste (inappropriate bulky waste) into a cylinder with holes of 400 mm.
- **Multi-stage trommel**: The waste is separated into small, medium and large size, using the first cylinder of 100 mm for the small fraction and a second of 300 mm for medium-sized, both normally containing organic matter. The large-sized waste continues to the end of the cylinders and it is disposed of.
- **Trommel 60:** Separates the waste through 60 mm in order to ensure a rich organic matter stream for the following processes.
- **Ballistic conveyor:** Consists of sloping paddles that allows separating the fine waste from the flat, light and rolling wastes that are removed of the system. Jointly with the small waste from the trommel, the fine waste is sent to wet pre-treatment. Electromagnets are employed to the small fractions that go into this pre-treatment to recover valuable material.
- **Pulper:** Incoming organic matter is mixed with recirculated water separating by flotation wastes like plastics and larger materials by decantation such as stone, glass or metallic splinters.
- **Hydrocyclones:** An upside-down water inlet at high speed separates the grit and other heavy and small material from the diluted organic waste, reproducing the movement of a cyclone.
- **Digester:** Constantly mixed and set up at 35 °C, for 20 days, anaerobic conditions are reached to decompose the organic matter by the present bacteria and produce biogas. This biogas will be stored into a gas storage tank. Then, mixed with air, combustion will lead enough force to the engine generator to produce electricity and heat.
- **Centrifuges (Solid-Liquid Separation):** Water is separated from organic matter which can be lately composted, dropping its humidity from 95% to 60%.

3.2 . FERMENTATION BATCH ASSAYS

Batch tests were conducted by triplicate in 250 mL glass bottles with 200 mL starting volume of MBT digester input and monitored between 20 and 30 days until the production was stabilized. Temperature was set in an incubator and controlled anaerobic conditions were achieved by flushing the headspace of the bottles with N_2 before they were sealed. The bottles were monitored by analyzing NH_4^+-N, pH, VFA and sCOD during all the experiment on 4 mL from each sampling event. During batch fermentation period, the pH in the bottles was not adjusted.

3.3. ANALYTICAL METHODS

The analyses protocols followed the Standard Methods for the Examination of Water and Wastewater [25] to guarantee the reliability and validity of the results obtained. The parameters assessed are shortly described below:

3.3.1. TOTAL SOLIDS (TS) AND TOTAL VOLATILE SOLIDS (TVS)

The concentration of TS (APHA 2540B) and TVS (APHA 2540D) is widely used to know the organic matter content of a sample. Following the next equation: Total Solids (TS) = Total Volatile Solids (TVS) + Total Fixed Solids (TFS), TS represents all solids contained in a sample, subdivided into the categories of TVS (those solids that are organic and will volatilize during combustion) and TFS (those solids that are Inorganic and thus will not volatilize during combustion). In the TS test, a measured weight of a sample is poured into a dry, weighed, nonflammable ceramic dish and dried at 105 ^{0}C during 24h in an evaporative oven (JP Selecta Conterm) until constant weight. Then, is reweighed when the dried dish has cooled to room temperature in a desiccator. Once the TS test is completed, the TVS is evaluated placing the dish in a muffle furnace (Oversal HD-230) set at 550 ^{0}C during 2 h and weighed at room temperature. TS and VS are expressed as a percentage of the sample and performed in triplicate.

3.3.2. CHEMICAL OXYGEN DEMAND (COD)

This assay is used in order to know the amount of oxygen required to oxidize the organic matter in a raw sample, under specific conditions of oxidizing agent and temperature. According to Standard Method 5220D, potassium dichromate is used to carry the oxidation in acid medium during 2 hours digestion (ECO 25 Thermoreactor), which indicates the determination of the parameter by the colorimetric method. The COD is calculated from the difference between the initially added and final potassium dichromate after oxidation, denoted from the ultraviolet-visible spectroscopy (Perkin Elmer Lambda 20) where the color variation produced by the reduction of Cr(VI) to Cr(III) is observed (orange to green).

The Chemical Oxygen Demand (COD) is defined as the amount of O_2 chemically equivalent to $Cr_2O_7^{2-}$ consumed in this process. This equivalence is established from the corresponding reduction-oxidation reactions in acid medium.

3.3.3. VOLATILE FATTY ACIDS (VFA)

To quantify VFA in a sample, it is centrifuged and filtered with a 0.45 µm syringe nylon filter. After dilution, 25 mL of phosphoric acid (H_3PO_4) is added for each mL of sample leaving it react. Then, the content is taken to a vial with a septum. The determination is carried out by gas chromatography (GC-2010 Plus, Shimadzu) equipped with a specific column (NukolTM 15m x 0.53mm) and a FID detector.

3.3.4. TOTAL AMMONIACAL NITROGEN (TAN):

TAN quantification is done using a selective ammonia electrode (Amonion Electrode, ORION), which is a gas-permeable hydrophobic membrane with an internal chloride electrode solution. The outer membrane of the electrode allows the transfusion of ammonia through it. The determination is based on the fact that the ammonium ion is converted to free ammonia by the addition of a caustic soda surplus following the next reaction:

$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O$ (Acid-base equilibrium between ammonium and ammonia)

4. RESULTS AND DISCUSSION

4.1. MBT PLANT PROCESS AND STREAM CHARACTERIZATION

Different streams samples of the plant have been collected and analyzed between January and June 2019. It is known that OFMSW is a seasonal heterogeneous residue. OFMSW characterization was akin to a similar substrate characterized by Cheah *et al.* [26], indicating some stability on these types of wastes composition. For these reasons, the results obtained during these months can provide relevant information of the potential related to MBT waste as a producer of VFA and its characteristics for possible future applications. Table 1 resumes the results obtained from the characterizations and the results are discussed below.

Table 1. Stream characterization of different streams collected periodically from MBT waste plant.

Day	Sample	TS (% w/w)	VS (% w/w)	VS/TS	VFA (mg/L)	sCOD (mgO_2/L)	pH	TAN (gNH_4^+-N/L)
16/01/19	*Digester inlet*	5.58 ± 0.05	4.07 ± 0.50	72.87 ± 0.21	6513		6.75	
	Pit Leachate				3050		5.35	
	Pulper outlet	6.60 ± 0.07	4.96 ± 0.01	75.04 ± 0.99	5034		6.01	
	Digester outlet	4.82 ± 2.18	1.93 ± 0.80	45.04 ± 22.03	819		8.11	
13/02/19	*Digester inlet*	5.83 ± 0.02	4,45 ± 0.04	76.39 ± 0.14	8052	39176 ± 952	6.62	2,19
	Pit Leachate				3287	99103 ± 7618	3.76	0,47
	Recirculation	2.55 ± 0.01	1,43 ± 0.05	56.06 ± 0.97	667	10727 ± 2143	8.51	2,66
	Pulper outlet	11.34 ± 0.10	9,01 ± 0.28	79.41 ± 1.75	6387	60049 ± 6190	5.58	1,74
	Digester outlet	3.60 ± 0.00	2,24 ± 0.03	62.24 ± 0.09	1126	14767 ± 238	8.38	2,71
26/02/19	*Digester inlet*	6.21 ± 0.27	4,77 ± 0.27	76,78 ± 0.99	9065	38151 ± 466	622	2,77
	Pit Leachate				2845	84116 ± 26794	4.02	0,53
	Recirculation	3.19 ± 0.10	1,69 ± 0.28	53,02 ± 1.76	1139	8496 ± 2330	859	3,18
	Pulper outlet	7.48 ± 0.49	5,95 ± 0.44	79,49 ± 0.64	4991	28101 ± 233	7.05	2,75
	Digester outlet	3.66 ± 0.01	2,32 ± 0.01	63,48 ± 0.31	1242	11461 ± 3262	8.33	3,22
19/03/19	*Digester inlet*	6.97 ±0,02	5.23 ± 0,04	74.99 ± 0.59	8902	48789 ± 1414	6.34	3,09
	Pit Leachate				2618	64983 ± 471	3.93	0,58
	Recirculation	2.82 ± 0,14	1.74 ± 0,09	61.92 ± 0.28	1459	16483 ± 1667	8.38	3,46
	Pulper outlet	7.62 ± 0,06	5.95 ± 0,06	78.08 ± 0.33	6222	41067 ± 430	6.50	3,29
	Digester outlet	3.99 ± 0,02	2.56 ± 0,01	64.13 ± 0.26	1895	14344 ± 1179	8.00	3,43
30/04/19	*Digester inlet*	7,02 ± 0,19	5,3 ± 0,24	75,43 ± 1.58	11668	55416 ± 471	6,55	2,64
	Pit Leachate				5859	96500 ± 838	4,01	0,84
	Recirculation	4,33 ± 0,03	2,7 ± 0,02	62,32 ± 0.23	1289	27583 ± 631	8,25	2,85
	Pulper outlet	8,87 ± 0,21	7,03 ± 0,18	79,26 ± 0.38	6730	67583 ± 235	6,17	2,13
	Digester outlet	3,4 ± 0,17	2,14 ± 0.10	62,74 ± 0.55	1288	36250 ± 3536	8,14	3,24

4.1.1. TS AND TVS ON THE MBT PLANT STREAMS

Represented on Figure 4, digester inlet and pulper outlet streams presented similar fraction of VS/TS (between 70-80%) for OFMSW. This percentage could be increased by the quality of the source-sorted collection of organic content and process configuration. Moreover, despite the fact that pulper outlet solids content is higher than the digester inlet because hydrocyclones remove solids, there is no influence on the VS/TS ratio, assuring an acceptable biodegradable content for anaerobic digestion.

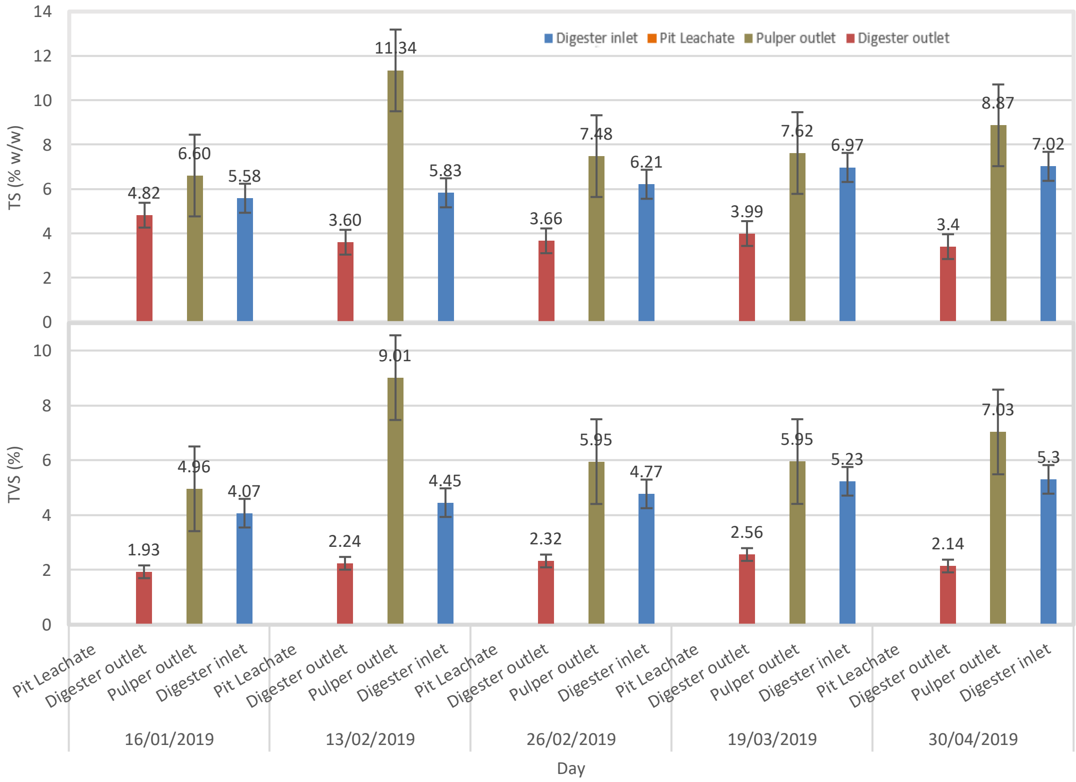

Figure 4. TS and TVS determination from MBT waste collected periodically.

Solids content on digester outlet is the lowest since AD reduce biodegradable organic matter and collect other solids at the bottom of the digester, where they are removed. One of the objectives of AD is to degrade the maximum biodegradable organic matter, as you can obtain more biogas from it and improve economic benefits.

4.1.2. VFA CONCENTRATION ON THE MBT PLANT STREAMS

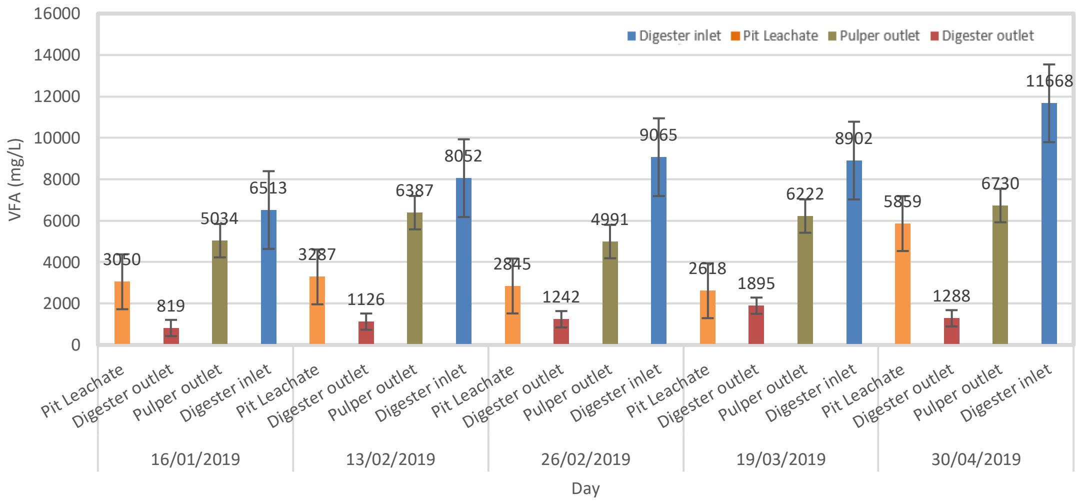

Figure 5. Total VFA determination from MBT waste collected periodically.

As can be observed in Figure 5, in most collections the own plant process and retention time fermented the stream before the digestion. For example, VFA content on digester inlet is higher than pulper outlet, indicating acidogenic fermentation while the streams are on the way from the pulper to the digester through the hydrocyclones.

Furthermore, pulper outlet is higher than the sum of the leachate plus digester outlet (similar to recirculation), so VFAs are also generated on the way of the pulper and into it. Additionally, the recirculation of the anaerobic digester supernatant into the pulper add VFAs and bacteria (hydrolytic, acidogenic, acetogenic) involved on the anaerobic digestion [27]. These bacteria contribution may increase hydrolysis rate and acidogenesis enhancing VFA production. Furthermore, pit leachate is a highly biodegradable stream which will be an additional substrate contributing to increase the VFA production. This is indicated on the difference between VFA content on the leachate and the pulper outlet so an amount of VFA is produced in the pulper. Is also remarkable how seasonality supposes a fermentation of the waste, showing higher VFA content on the digester inlet as the temperatures get higher from January to May.

4.1.3. EVALUATION OF sCOD ON THE MBT PLANT STREAMS

Higher sCOD levels indicate a greater amount of oxidizable organic material in the sample that can be converted into VFA. Usually, more substrate can be converted into

VFAs when hydrolysis is not needed but it will depend on the substrate complexity, microorganisms activity and inhibitors presence. This experience is shown on pit leachate stream. This biodegradable organic stream has the highest sCOD but is still fresh and cannot be totally hydrolyzed so it is not enriched in VFA contrasted with other streams such as digester inlet or pulper outlet. This factor could be related with the required time of hydrolysis and fermentation to convert the complex COD into VFA. As it has happened on VFA content examination, sCOD is diminished after anaerobic digestion and seasonality involves more sCOD in the digester inlet or pit leachate. Most of all, pulper outlet had a higher sCOD than digester inlet. Hydrocyclones may remove liquid and impurities reducing sCOD but soluble compounds should be uniform across the liquid stream.

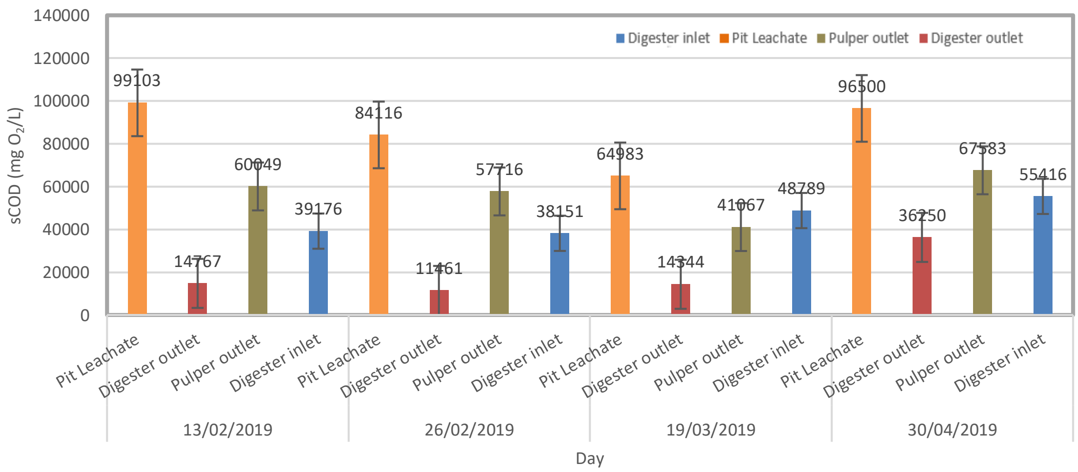

Figure 6. sCOD determination from MBT waste collected periodically.

4.1.4. EVALUATION OF pH AND TOTAL AMMONIACAL NITROGEN (TAN) ON THE MBT PLANT STREAMS

MBT waste streams are frequently characterized to have an initial pH between 6 and 7. The pH determination can provide relevant information about microorganisms metabolic activity since acidogens have been reported to work better on pH around 6. Pit leachate is dominated for high biodegradable organic matter but lower ammonium content. Organic matter decomposition generates volatile fatty acids, lactic acid, etc.

reducing the pH (see Figure 7). It was not found a significant difference between digester inlet and pulper outlet. This could be related with the recirculation of the supernatant from anaerobic digestion which has pH between 8 and 9, and an alkalinity > 10 $gCaCO_3/L$, supplementing a large buffer capacity.

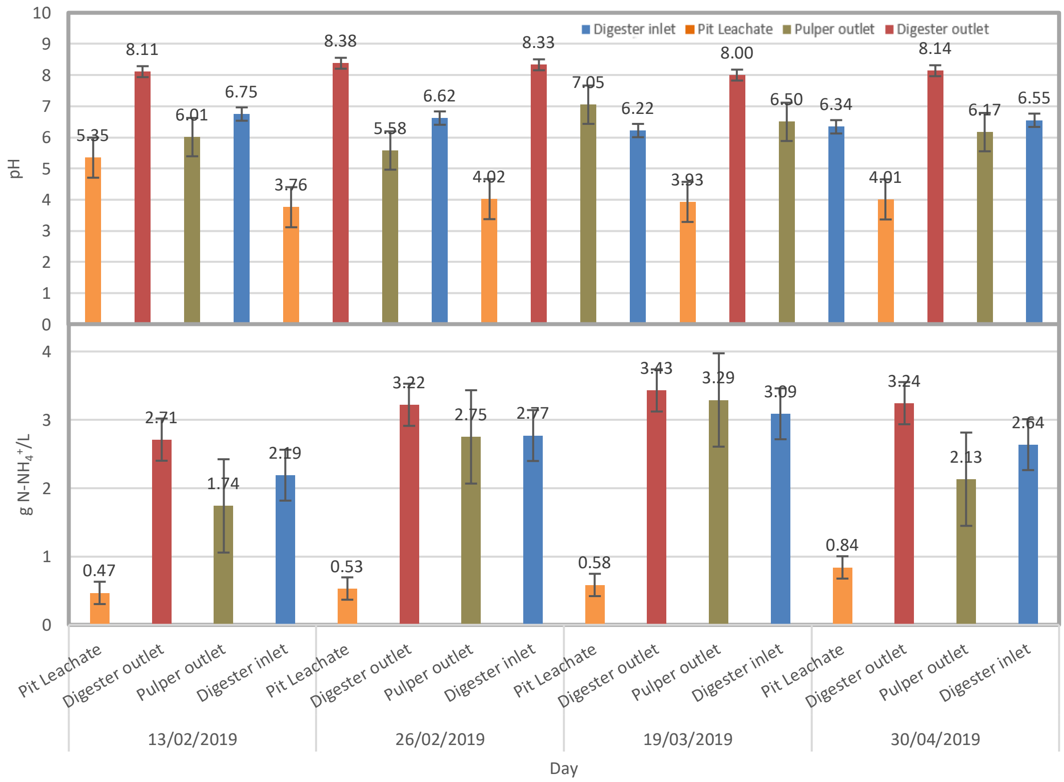

Figure 7. pH and Total Ammoniacal Nitrogen determination from MBT waste collected periodically.

Represented in Figure 7, nitrogen content was also increased along the process. During anaerobic digestion, organic matter is hydrolyzed increasing ammoniacal nitrogen in the medium. Pulper outlet and digester inlet have no significant variability. However, pit leachate has the lower N content (< 1 g $N\text{-}NH_4^+/L$), organic matter leachate is typically characterized to have a lack of nutrients. The values obtained from MBT waste after anaerobic digestion at 35 ^{o}C were slightly lower than the values obtained by Pantini *et al.* [28] which were 4.2 ± 0.2 and 4.2 ± 0.3 in samples removed from anaerobic batch reactors at 37 ^{o}C.

4.2. FERMENTATION BATCH ASSAYS: VFA YIELD AND PROFILE

The anaerobic digester inflow was used on fermentation assays to determine the VFA yield for each sample, as well as the speciation of the VFA produced (Figure 8). Previous investigations have been performed anaerobic digestion experiments [28, 29, 30] and VFAs production from OFMSW [13,20]. In this study five experiments were carried out under mesophilic conditions (35 ^{o}C) and four profiles in other temperatures, i.e. 20, 45, 55, and 70 ^{o}C. The aim of these assays was to observe if there is reproducibility within profiles and evaluate how temperature influences VFA production on MBT waste. Previous literature reported that mesophilic conditions had advantages over thermophilic on VFA production, not only for the related cost but also due to higher process stability and more solubility of carbon dioxide [31]. In addition, higher temperatures involve higher concentration of ammonia which can easily hinder methanogenic activity [32,33].

Firstly, will be shown the batch assays performed at 35 ^{o}C, in order to be compared with the different temperature conditions on the following section. Each assay corresponds to one single collection day and the VFA production is expressed as mg COD_{VFA}/L and mg COD_{VFA}/gVS initially added to see the specific production related with the organic matter added into the sample.

Showed on Annex I and Annex II, pH and nitrogen concentration were also monitored. Ammoniacal nitrogen was between 3.83 and 4.87 mg $N\text{-}NH_4^+$/L after fermentation assays, higher in contrast with Jiang *et al.* [19] fermenting food waste due to MBT waste has an increase of total ammoniacal nitrogen from the anaerobic digester recirculation. The pH at 35 ^{o}C varied within 5.8 and 7.05 depending on the sample and increasing with the time. Besides, also found by He *et al.* [34], pH had the biggest drop during the first day. Along with the reaction, pH still suffered a smaller drop and after 4 or 5 days was kept regular. Organic acids generated through this process caused the decrease of pH. Organic acids release through organic matter degradation caused the decrease of the pH. Consequently, higher VFA production produced higher pH drop.

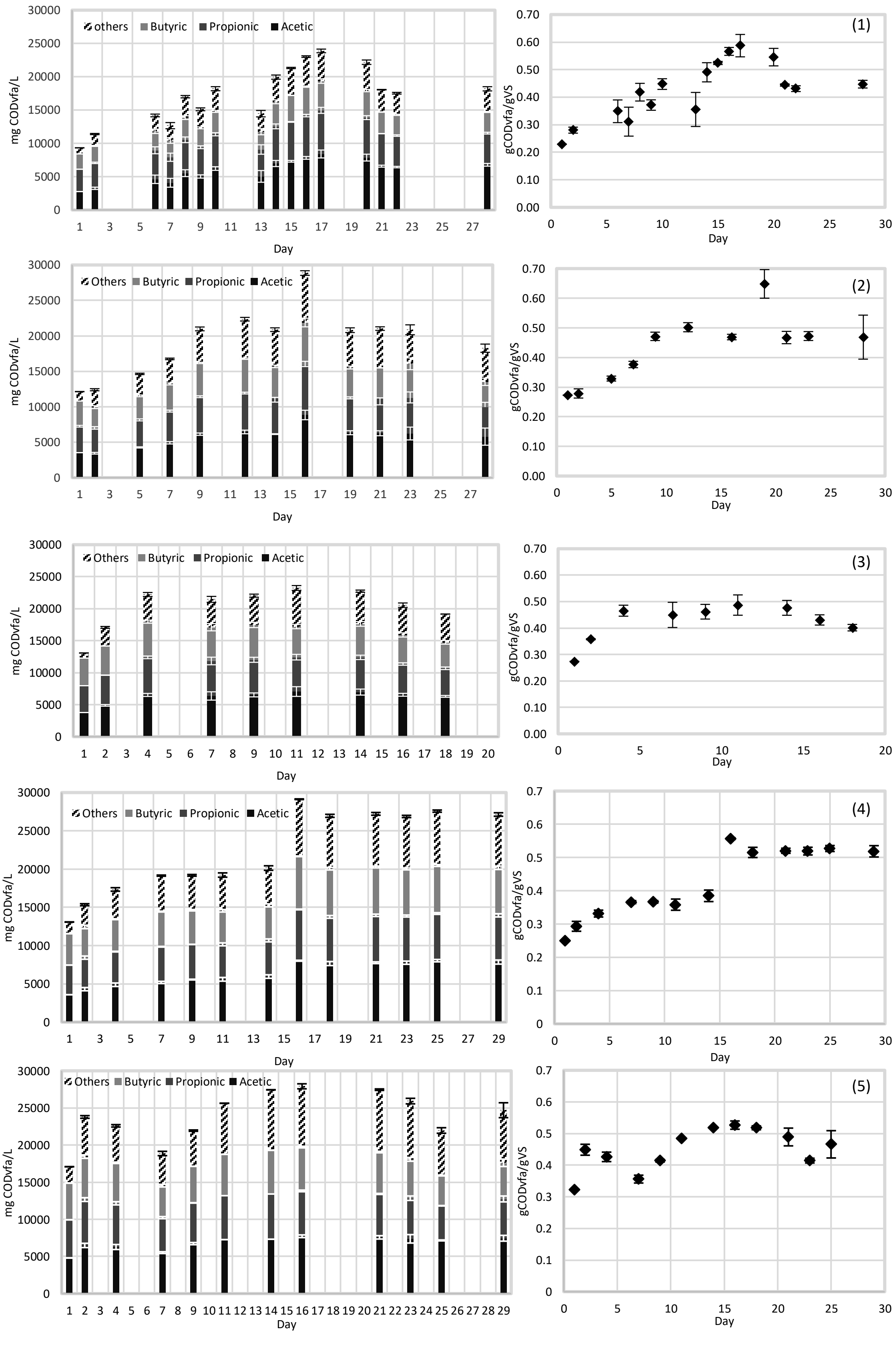

Figure 8. Daily monitoring profiles of VFA production at 35 °C on batch assays by triplicate: 1 (16/01/2019), 2 (13/02/2019) 3 (26/02/2019), 4 (19/03/2019) and 5 (30/04/2019).

In Figure 8, it can be appreciated that there is a tendency on the profiles and VFA production yields. On all profiles, the peak production was between 14 and 17 days with maximum of 29.13 g COD_{VFA} /L and all assays produced a maximum within 20 g COD_{VFA} /L and 30 g COD_{VFA} /L. These results are higher than the reported by Garcia-Aguirre *et al.* [17] who obtained 8 g COD_{VFA}/L produced from OFMSW in 10 days. On Profile 3, the peak is on 11 days, this may be related to pre-fermentation of the sample before collection. Thus, the profile will be found on a different profile point of degradation, even though the trend is the same. Otherwise, a ratio of 0.318 gVFA/gVS_{fed} yield in 9 days reached to a maximum of 0.441 gVFA/gVS_{fed} in 16 days, which was slightly lower than 0.379 g/gVS_{fed} obtained by Jiang *et al.* [19] in 8 days at similar operating conditions but in concordance with the specific production achieved by Moretto *et al.* [18] fermenting urban waste (0.5-0.6 $gCOD_{VFA}$/gVS). Even that a tendency is recognized within food wastes VFA production, differences in substrate composition influences the VFA potential production and speciation [35].

Overall, at same operational conditions, total VFAs concentrations obtained at 35 ^{o}C were higher than those reported by Dahiya *et al.* [15], Komemoto *et al.* [36] and Lim *et al.* [37] and lower than 41.34 g VFA/L reached by Jiang *et al.* [19] probably by cause of a higher VS content on the source.

Nevertheless, after 16 or 17 days, the production was stabilized probably due to substrate limitation. As literature concerns, longer HRT allows better degradation of the substrate by microorganisms [38]. Zhou *et al.* [16] found out that HRTs until 12 days can improve VFA production and process stability with complex substrates such as OFMSW. A similar case was experienced by Lim *et al.* [37] with no significant VFAs production improvement between 8 and 12 days.

4.2.1. FERMENTATION BATCH ASSAYS: VFA YIELD AND PROFILE WITH TEMPERATURE CONDITION

In order to assess the temperature effect on VFA production on MBT waste, batch assays were performed at 20, 45, 55 and 70 ^{o}C and was carried out one profile at 35 ^{o}C as control for each assay. Previously stated, temperature is an important operational factor to improve VFA production. The first assay was set at 35, 20 and 45 ºC and the second at 35, 55 and 70 ºC. Table 2 summarize the results exhibited on Figure 9.

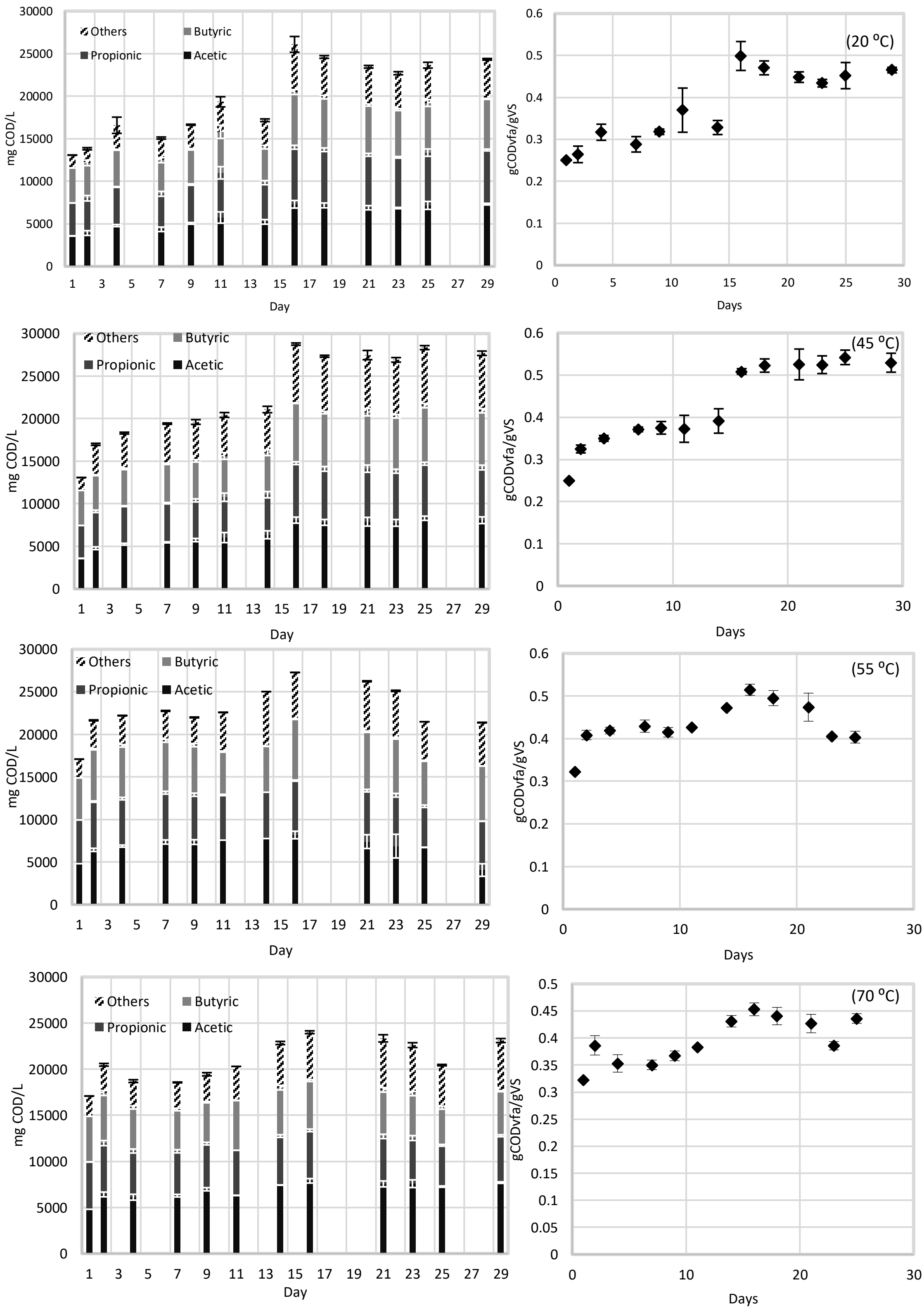

Figure 9. Daily monitoring profiles of VFA production (mg VFA/L) on batch assays by triplicate: 20 ºC (19/03/2019), 45 ºC (19/03/2019), 55 ºC (30/04/2019), 70 ºC (30/04/2019).

On the next table are summarized the results from fermentation assays of MBT waste at different temperature:

Table 2. Effects of temperature on pH, ammonia and VFAs production from MBT waste.

Day	Sample	Initial pH	Final pH	Initial $N\text{-}NH_4^+$ (g/L)	Final $N\text{-}NH_4^+$ (g/L)	Max. CODvfa (g/L)	gCODvfa/gVS	COD_{VFA}(Ac,But, Prop)/$sCOD_{VFA}$(%)*
19/03/19	35 ºC	6.34	5.84	3.09	4.60	29.13 (Day 16)	0.557	74
	20 ºC	6.34	5.98	3.09	4.02	26.10 (Day 16)	0.499	81
	45 ºC	6.34	6.23	3.09	4.80	28.76 (Day 16)	0.542	76
30/04/19	35 ºC	6.55	6.49	2.64	4.59	27.92 (Day 16)	0.527	71
	55 ºC	6.55	6.91	2.64	4.61	27.28 (Day 16)	0.515	76
	70 ºC	6.55	7.18	2.64	5.09	24.01 (Day 16)	0.453	76

* This ratio was determined to assess which amount of COD was due to the mainly produced acids from this type of waste.

As can be noted at the previous table, 35 ºC accumulated the largest VFAs production and specific VFA production, followed by 45, 55, 20 and 70 ºC. From 35 ºC, the higher temperature condition, the less VFA production was obtained. Similar results were achieved by [19,34,36] increasing the temperature for VFA production enhancement. The hyperthermophilic range (70 ºC) seems to decrease acidogenic bacteria metabolism resulting on less VFA production, also experimented by He *et al.* [34] where thermophilic temperatures decreased VFA total production under acidic uncontrolled pH. Several acidogens cannot survive at hyperthermophilic temperatures surpassing acidogenic bacteria optimal bacterial growing temperature [20]. However, hyperthermophilic ranges can be interesting since it supposes an effective pathogen removal on the final product providing higher organic matter sanitation. Nevertheless, 20 ºC is not considered as a suitable operational temperature since VFA production can decrease notably. Reported by Lim *et al.* [37] at 25 ºC, a lower VFA production was found when the temperature was lower than 35 ºC. Concerning maximum VFA concentration, VFA production kinetics seems to be favored in acidic conditions and mesophilic temperature. Taken together, these data show that VFAs production was highest at 35 ºC, even that was slightly similar to 45 and 55 ºC, in contrast with Jiang *et al.* [19] who found the maximum at 45 ºC. Anyway, less energy will be needed to produce the same amount of VFA.

Represented on Annex I and Annex II, throughout the complete batch test, pH was stable at 35 ^{o}C from day 4 to 25 and slightly varied at higher temperatures. This stability may be cause of a high alkalinity added from the recirculation (> 10 g $CaCO_3$/L) of the anaerobic digester of the plant, in contrast with [19,20] where uncontrolled pH reactors dropped quickly to pH below 3. The effluent from anaerobic digester adds active microbial population which facilitate the degradation of the organic matter and alleviate VFA inhibition in the system [24, 39]. Also observed by Xu *et al.* [40] higher pH and temperature leads to a higher release of ammonia, so the particulate nitrogen can be easily hydrolyzed. As notified He *et al.* [34], pH decreasing range at 35 ^{o}C was higher than that at 55 and 70 ^{o}C.

Found also by Dahiya *et al.* [15] and Jiang *et al.* [19], among the carboxylic acids, acetic acid, followed by butyric acid and propionic acid were the most produced acids in all tests and represented above 80% of the total acid speciation. Besides experimented by Jiang *et al.* [19], acetate and butyrate accounted for 60% of the total VFAs. Showed above on Table 2 and represented on Annex III and Annex IV, The COD due to acetic, butyric and propionic acid was evaluated among the total COD with temperature condition. The first day was found the maximum variation and then after 5 days the speciation remained stable as happened with the pH. Showed on Annex III and Annex IV, at 35 ^{o}C all profiles were dominated by acetic acid, followed by propionic and butyric acid. Then, valeric and caproic acid at lower concentrations. Similar happened at 70 and 20 ^{o}C. However, at 45 and 55 ^{o}C, butyric acid represented a higher percentage than propionic acid, even that the differences between profiles were slightly similar. At 20 ^{o}C was the higher COD_{VFA}/sCOD ratio which indicates that larger acids were less produced. Even that at 35 ^{o}C the ratio was lower than at 45, 55 and 70 ^{o}C the differences were insignificant. In all cases the COD_{VFA} due to large chain fatty acids (> C_4) was due to valeric and caproic acid within the 50 and 60% of the total.

4.2.2. FERMENTATION BATCH ASSAYS: COD_{VFA}/sCOD RATIO

The relation between COD_{VFA}/sCOD (Figure 10) shows how effective is acidogenesis producing VFA as a part of total sCOD since are used as a carbon source in diverse biological processes [19]. Soluble monomers are released from complex molecules as primary products of hydrolysis and these are measured as sCOD. The sCOD is normally divided into: complex soluble COD (csCOD) and COD_{VFA}. However, in biological systems is important to pay attention on optimal temperature activity range or bacterial activity will be decreased. Figure 10 shows the variation of sCOD on the different fermentation assays at 35 ^{o}C.

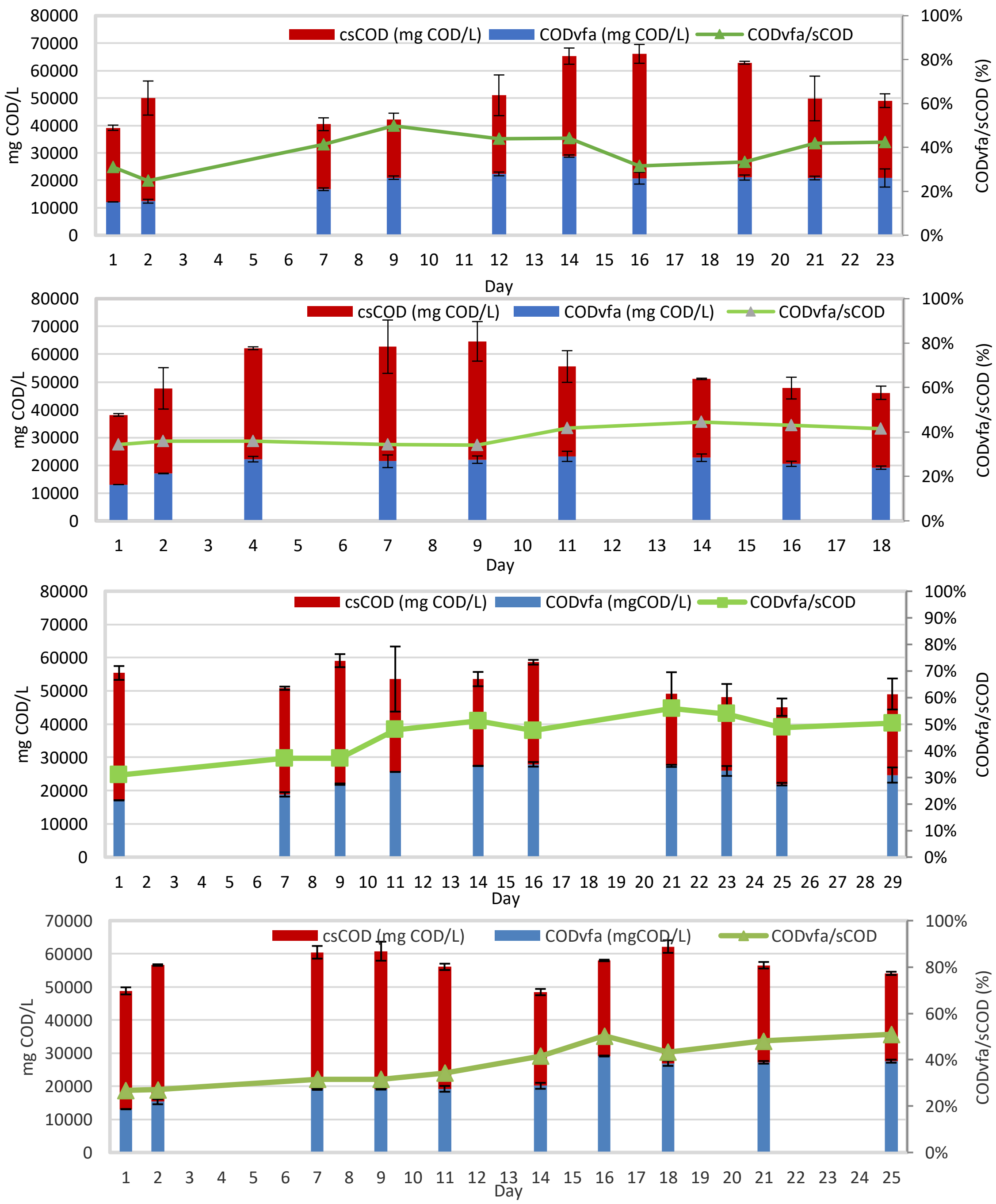

Figure 10. Ratio COD_{VFA}/sCOD representation obtained on 35 ^{o}C on batch assays by duplicate for profiles: 2 (13/02/2019) 3 (26/02/2019), 4 (19/03/2019) and 5 (30/04/2019), respectively.

In these cases, a maximum production between 60 and 70 g COD/L was achieved, which is boosted compared with [36,37]. However, Jiang *et al.* [19] achieved 85 g/L fermenting food waste at 35 ^{o}C, maybe due to a higher biodegradable substrate which allow a higher solubilization of the sample.

Related to the COD_{VFA}/sCOD rate, a maximum percentage of 56% was achieved. These results are remarkably higher respect the 6.6% obtained by Jiang *et al.* [19] also at uncontrolled pH probably due to a worse process stability. On most assays performed, sCOD increases with HRT the first days and after dropped notably in contrast with Komemoto *et al.* [36] which at 35 ^{o}C remained stable once the maximum was reached.

4.2.3. FERMENTATION BATCH ASSAYS: COD_{VFA}/sCOD WITH TEMPERATURE CONDITION

As mentioned in Section 1.4.1. organic residues present limited hydrolysis step, increasing the temperature expect to improve hydrolysis rate and gain soluble matter in the sample. However, working on high temperatures involve a higher energy system consumption. Moreover, the following table summarize the results obtained on Figure 11 which represents the sCOD and the ratio COD_{VFA}/sCOD from batch assays at different temperatures (20, 45, 55 and 70 ^{o}C) to be compared with 35 ^{o}C:

Table 3. Effects of temperature on sCOD and CODvfa/sCOD production from MBT waste

Day	Sample	sCOD (g/L)	COD_{VFA}/sCOD
19/03/2019	*35 ℃*	63.11	54
	20 ℃	54.65	50
	45 ℃	63.35	50
30/04/2019	*35 ℃*	59.12	56
	55 ℃	62.35	53
	70 ℃	98.32	41

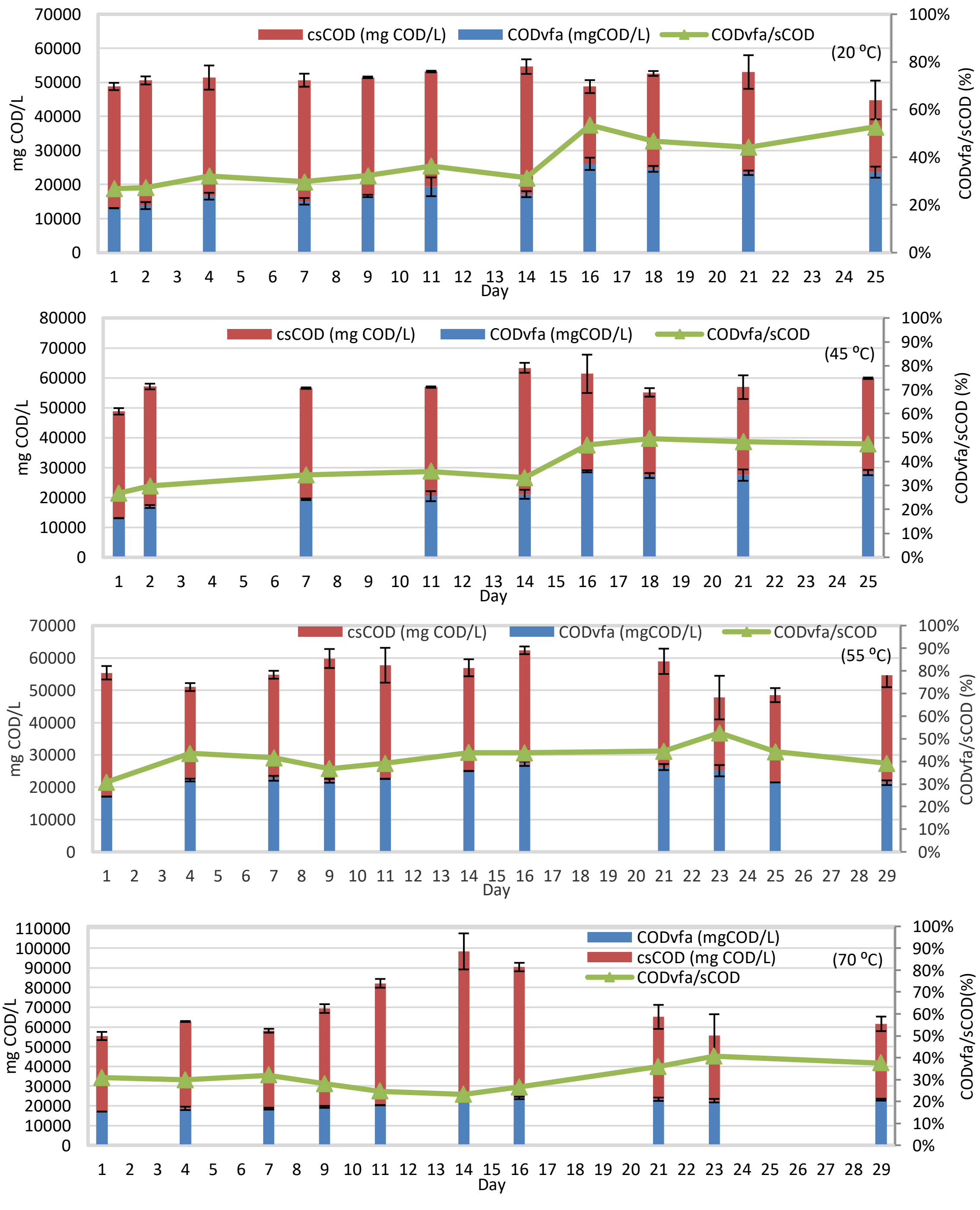

Figure 11. Ratio COD_{VFA}/sCOD representation obtained on batch assays by duplicate with temperature variation: 20 ºC (19/03/2019), 45 ºC (19/03/2019), 55 ºC (30/04/2019) and 70 ºC (30/04/2019).

Working on high range temperatures enhance hydrolysis rate and led to increase soluble and accessible matter for microorgasims [15] ruled by chemical-physics effects, while in mesophilic range will be lower as the enzyme activity is predominant [12]. As experienced at 35 ºC, on mesophilic and especially thermophilic temperatures, sCOD increased quickly on the first days due to physicochemical effects and days after dropped slightly for 45 and 55 ^{o}C and dropped remarkably at 70 ^{o}C. However, the thermophilic profile presented the higher sCOD along all the batch assay (> 60 g COD/L).

Overall, the maximum sCOD was produced between day 14 and 16 in contrast to He *et al.* [34] who achieved maximum yields on 3 and 5 days for 35, 55 and 70 ^{o}C. This may be related on that OFMSW is more complex substrate than FW requiring more time to get hydrolyzed [26]. Even that higher temperature hydrolyzed more organic matter since day 1, it needed similar days to achieve the maximum than the other profiles. After peak production, sCOD started to decrease while VFA production was remaining on the highest points (see Section 4.2.2), indicating that since this point acidification rate was higher than hydrolysis.

Jiang *et al.* [19] and Komemoto *et al.* [36] previously mentioned that sCOD concentration increased as temperature increased and the ratio of COD_{VFA}/ sCOD decreased, so the organic matter solubilized is not converted greatly into VFAs. At 20 ^{o}C the lowest values of sCOD were found and no significant increase of sCOD was appreciated. This suggest that low temperatures cannot facilitate biological activity and hydrolysis. Stability on sCOD production was achieved at 45 and 35 ^{o}C until the end of the experiment suggesting that microorganisms action at this point was limited or there was a lackage of inoculum. Also reported by Jiang *et al.* [19], thermophilic temperatures decrease the COD_{VFA}/sCOD ratio since hydrolysis extent is larger but acidogens are limited at high ranges temperatures, then VFA production is lower.

5. CONCLUSIONS

MBT waste has great potential for VFA production. Temperature had a significant influence on fermentation yield but not on VFA speciation. Different temperatures (20, 45, 55 and 70 ^{o}C) were evaluated and compared with 35 ^{o}C on batch assays. These results give feasible information for MBT waste on VFAs production in order to valorize specific wastes on alternative processes. The analysis confirmed that can be reproducibility on the results obtained: the highest peak production was repeatedly obtained at 35 ^{o}C between 14 and 17 days with a maximum of 29 g COD_{VFA} /L. Different temperature assays produced a maximum within 20 g COD_{VFA} /L and 30 g COD_{VFA} /L under pH between 6 and 7. At 35 ^{o}C was accumulated the largest VFAs production and specific VFA production, followed by 45, 55, 20 and 70 ^{o}C, indicating lower feasibility at psychrophilic and thermophilic temperatures. Acetic, butyric and propionic acids were the most produced acids in all the profiles (within 70 and 80% of total COD_{VFA}) and 35 ^{o}C allowed the higher conversion of sCOD into large acid carbon chains (>C4).

Furthermore, both the ratio COD_{VFA}/sCOD and specific production ($gCOD_{VFA}$/gVS) decreased as temperature increased even that the differences at 45 and 55 ^{o}C from 35 ^{o}C were slight. Nevertheless, 20 ^{o}C resulted to be an unfeasible temperature for VFAs production. At 70^{o}C, even that it was the assay that presented more sCOD, the production was lower. The concentrations of NH_4^+-N and pH increased as temperature increased due to higher ammoniacal nitrogen and lower carbon dioxide solubility.

The achievements of this investigation could generate an alternative for biorefinery innovations and valorization of OFMSW, focused on obtaining valuable bio-products using manageable and feasible methods.

6. REFERENCES

[1] Mata-Álvarez, J., Macé, S., Llabrés, P. (2000). Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. *Bioresource Technology*, 74, 2–16.

[2] Food and Agriculture Organization of the United Nations (FAO) [online]. [consulted: 01/02/2019]. Available in: http://www.fao.org/food-loss-and-food-waste/en/

[3] Judit Monjo Pastor (2014). Estudi de la Composició dels Residus Municipals de Catalunya, Departament Entorn Ambiental Urbà. [online]. [consulted: 06/03/2019]. Available on: http://residus.gencat.cat/web/.content/home/actualitat/2014/1211_composicio_brossa/Estudi-de-la-composicio-dels-Residus-Municipals-de-Catalunya.pdf

[4] Morin, P., Marcos, B., Moresoli, C., Laflamme, CB. (2010). Economic and environmental assessment on the energetic valorization of organic material for a municipality in Quebec, Canada. *Applied Energy*, 87, 275–83.

[5] Malinauskaite, J., Jouhara, H., Czajczynska, D., Stanchev, P., Katsou, E., Rostkowski, P., Thorne, R. J., Colón, J., Ponsá, S., Al-Mansour, F., Anguilano, L., Krzyzynska, R., López, I.C., Vlasopoulos, A., Spencer, N. (2017). Municipal solid waste management and waste-to-energy in the context of a circular economy and energy recycling in Europe. *Energy*, 141, 2013-2044. https://doi.org/10.1016/j.energy.2017.11.128

[6] Ducom, G., Achour, F., Rouez, M., Bayard, R., Arau, J. De. (2008). Mass balance to assess the efficiency of a mechanical – biological treatment. (2008). *Waste Management*, 28, 1791–1800.

[7] Murphy, J.D., McKeogh, E., Kiely, G. (2004). Technical, economic and environmental analysis of energy production from municipal solid waste. *Applied Energy*, 77, 407-427.

[8] Hilkiah Igoni, A., Ayotamuno, M. J., Eze, C. L., Ogaji, S. O. T., Probert, S. D. (2008) Designs of anaerobic digesters for producing biogas from municipal solid-waste. *Applied Energy*, 85, 430–438.

[9] Romero-Güiza, S. M., Mata-Alvarez, J., Chimenos, J. M., Astals, S. (2016). Nutrient recovery technologies for anaerobic digestion systems: An overview. *ION*, **29**(1), ISSN 0120-100X

[10] Strazzera, G., Battista, F., Garcia, N. H., Frison, N., Bolzonella, D. (2018). Volatile fatty acids production from food wastes for biorefinery platforms: A review. *Journal of Environmental Management*, 226, 278–288. https://doi.org/10.1016/j.jenvman.2018.08.039

[11] Atasoy, M., Owusu-agyeman, I., Plaza, E., Cetecioglu, Z. (2018). Bioresource Technology Bio-based volatile fatty acid production and recovery from waste streams: Current status and future challenges. *Bioresource Technology*, 268, 773–786. https://doi.org/10.1016/j.biortech.2018.07.042

[12] Lee, W.S., Chua, A.S.M., Yeoh, H.K., Ngoh, G.C. (2014). A review of the production and applications of waste-derived volatile fatty acids. *Chemical Engineering Journal*, 235 83-99.

[13] Bastone, D.J., Keller, J., Angelidaki, I., Kalyuzhnyi, S.V., Pavlostathis, S.G., Rozzi, A., Sanders, W.T.M., Siegrist, H., Vavilin, V.A. (2002). Anaerobic Digestion Model No. 1 (ADM1). *IWA*, **45**(10), 65-73.

[14] Mohan, S. V. (2009). Harnessing of biohydrogen from wastewater treatment using mixed fermentative consortia: Process evaluation towards optimization. *International Journal of Hydrogen Energy*, **34**(17), 7460–7474.

[15] Dahiya, S., Sarkar, O., Swamy, Y. V., Mohan, S. V., (2015). Acidogenic fermentation of food waste for volatile fatty acid production with co-generation of biohydrogen. *Bioresource Technology*, 182, 103–113.

[16] Zhou A. J., Yang C. X., Guo Z. C., Hou Y. N., Liu W. Z., Wang A. J., (2009). Volatile fatty acids accumulation and rhamnolipid generation in situ from waste activated sludge fermentation stimulated by external rhamnolipid addition. *Biochemical Engineering Journal*, 77, 240–245.

[17] Garcia-Aguirre, J., Aymerich, E., Goñi, J. G., Esteban-Gutiérrez, M. (2017). Selective VFA production potential from organic waste streams: Assessing temperature and pH influence. *Bioresource Technology*, 244, 1081–1088.

[18] Moretto, G., Valentino, F., Pavan, P., Majone, M., Bolzonella, D. (2019). Optimization of urban waste fermentation for volatile fatty acids production. *Waste Management*, 92, 21–29. https://doi.org/10.1016/j.wasman.2019.05.010

[19] Jiang, J., Zhang, Y., Li, K., Wang, Q., Gong, C., Li, M. (2013). Volatile fatty acids production from food waste: Effects of pH, temperature, and organic loading rate. *Bioresource Technology*, 143, 525–530.

[20] Shin, H.S., Youn, Y.H., Kim, S.H. (2004). Hydrogen production from food waste in anaerobic mesophilic and thermophilic acidogenesis. *International Journal of Hydrogen Energy*, 29, 1355–1363.

[*21*] Rebecchi, S., Pinelli, D., Bertin, L., Zama, F., Fava, F., Frascari, D. (2016). Volatile fatty acids recovery from the effluent of an acidogenic digestion process fed with grape pomace by adsorption on ion exchange resins. *Chemical Engineering Journal,* 306, 629–639. *https://doi.org/10.1016/j.cej.2016.07.101*

[22] Granda, C. B., Holtzapple M. T., Luce G., Searcy K., Mamrosh, D. L. (2009). Carboxylate platform: The MixAlco process part 2: Process economics. Applied Biochemistry and Biotechnology, 156, 107–124.

[23] Valentino, F., Beccari, M., Fraraccio, S., Zanaroli, G., Majone, M., 2014. Feed frequency in a Sequencing Batch Reactor strongly affects the production of polyhydroxyalkanoates (PHAs) from volatile fatty acids. *New Biotechnology*, 31, 264–275. https://doi.org/10.1016/j.nbt.2013.10.006

[24] Shen, L., Hu, H., Ji, H., Cai, J., He, N., Li, Q., Wang, Y., 2014. Production of poly(hydroxybutyrate – hydroxyvalerate) from waste organics by the two stage process: focus on the intermediate volatile fatty acids. *Bioresource Technology*, 166, 194–200.

[25] APHA (2017) Standard methods for the examination of water and waste water, 23rd edition. American Public Health Association, American Water Association and Water Environment Federation, Washington, DC [consulted: 09/02/2019].

[26] Cheah, Y., Vidal-antich, C., Dosta, J., Mata-Alvarez, J. (2019). Volatile fatty acid production from mesophilic acidogenic fermentation of organic fraction of municipal solid waste and food waste under acidic and alkaline pH. *Environmental Science and Pollution Research*. https://doi.org/10.1007/s11356-019-05394-6

[27] Zuo, Z., Wu, S., Zhang, W., Dong, R. (2013). Effects of organic loading rate and effluent recirculation on the performance of two-stage anaerobic digestion of vegetable waste. *Bioresource Technology*, 146, 556–561. https://doi.org/10.1016/j.biortech.2013.07.128

[28] Pantini, S., Verginelli, I., Lombardi, F., Scheutz, C., Kjeldsen, P. (2015). Assessment of biogas production from MBT waste under different operating conditions. *Waste Management*, 43, 37–49. https://doi.org/10.1016/j.wasman.2015.06.019

[29] Di Lonardo, MC, Binner, E., Lombardi, F., 2014. Investigation on biological stability degree of mechanically–biologically pre-treated MSW produced in Rome. *In: Eurasia Waste Management Symposium*.

[30] Sormunen, K., Einola, J., Ettala, M., Rintala, J. (2008). Leachate and gaseous emissions from initial phases of landfilling mechanically and mechanically – biologically treated municipal solid waste residuals, *Bioresource Technology*, 99, 2399–2409. https://doi.org/10.1016/j.biortech.2007.05.009

[31] Barrena, R., Imporzano, G., Pons, S., Gea, T., Artola, A., Vázquez, F., Sánchez, A., Adani, F. (2009). In search of a reliable technique for the determination of the biological stability of the organic matter in the mechanical – biological treated waste. *Journal of hazardous materials,* 162, 1065–1072. https://doi.org/10.1016/j.jhazmat.2008.05.141

[32] Gallert, C., Winter, J. (1997). Mesophilic and thermophilic anaerobic digestion of source-sorted organic wastes: Effect of ammonia on glucose degradation and methane production. *Applied Microbiology and Biotechnology*., **48**(3), 405–410.

[33] Braun, R., Hubert, P., Meyrath, J. (1981). Ammonia toxicity in liquid piggery manure digestion. *Biotechnology Letters*, **3**(4), 159-164.

[34] Mata-Alvarez, J., Dosta, J., Macé, J., Astals, S. (2011). Codigestion of solid wastes: A review of its uses and perspectives including modeling. *Critical Reviews in Biotechnology*, **31**(2), 99-111.

[35] He, M., Sun, Y., Zou, D., Yuan, H., Zhu, B., Li, X., Pang, Y., (2012). Influence of temperature on hydrolysis acidification of food waste. *Procedia Environmental Science*, 16, 85–94.

[36] Komemoto, K., Lim, Y.G., Nagao, N., Onoue, Y., Niwa, C., Toda, T. (2009). Effect of temperature on VFA's and biogas production in anaerobic solubilization of food waste. *Waste Management*, **29** (12), 2950–2955

[37] Lim S., Kim B. J., Jeong CM., Choi J., Ahn Y. E., Chang H. N. (2008). Anaerobic organic acid production of food waste in once-a-day feeding and drawing-off bioreactor. *Bioresource Technology,* 99, 7866–7874

[38] Bengtsson, S., Hallquist, J., Werker, A., Welander, T. (2008). Acidogenic fermentation of industrial wastewaters: Effects of chemostat retention time and pH on volatile fatty acids production. *Biochemical Engineering Journal*, 40, 492–499. https://doi.org/10.1016/j.bej.2008.02.004

[39] Zhang, B., He, P., Lü, F., Shao, L., Wang, P. (2007). Extracellular enzyme activities during regulated hydrolysis of high-solid organic wastes. *Water Research*, 41, 4468–4478. https://doi.org/10.1016/j.watres.2007.06.061

[40] Xu, S.Y., Lam, H.P., Karthikeyan, O.P., Wong, J.W.C. (2011). Optimization of food waste hydrolysis in leach bed coupled with methanogenic reactor: effect of pH and bulking agent. *Bioresource Technology*, **102**(4), 3702–3708.

ANNEXES

<u>ANNEX I:</u> Below is represented the pH and initial/final ammonia concentration monitored on profiles at 35 ^{o}C.

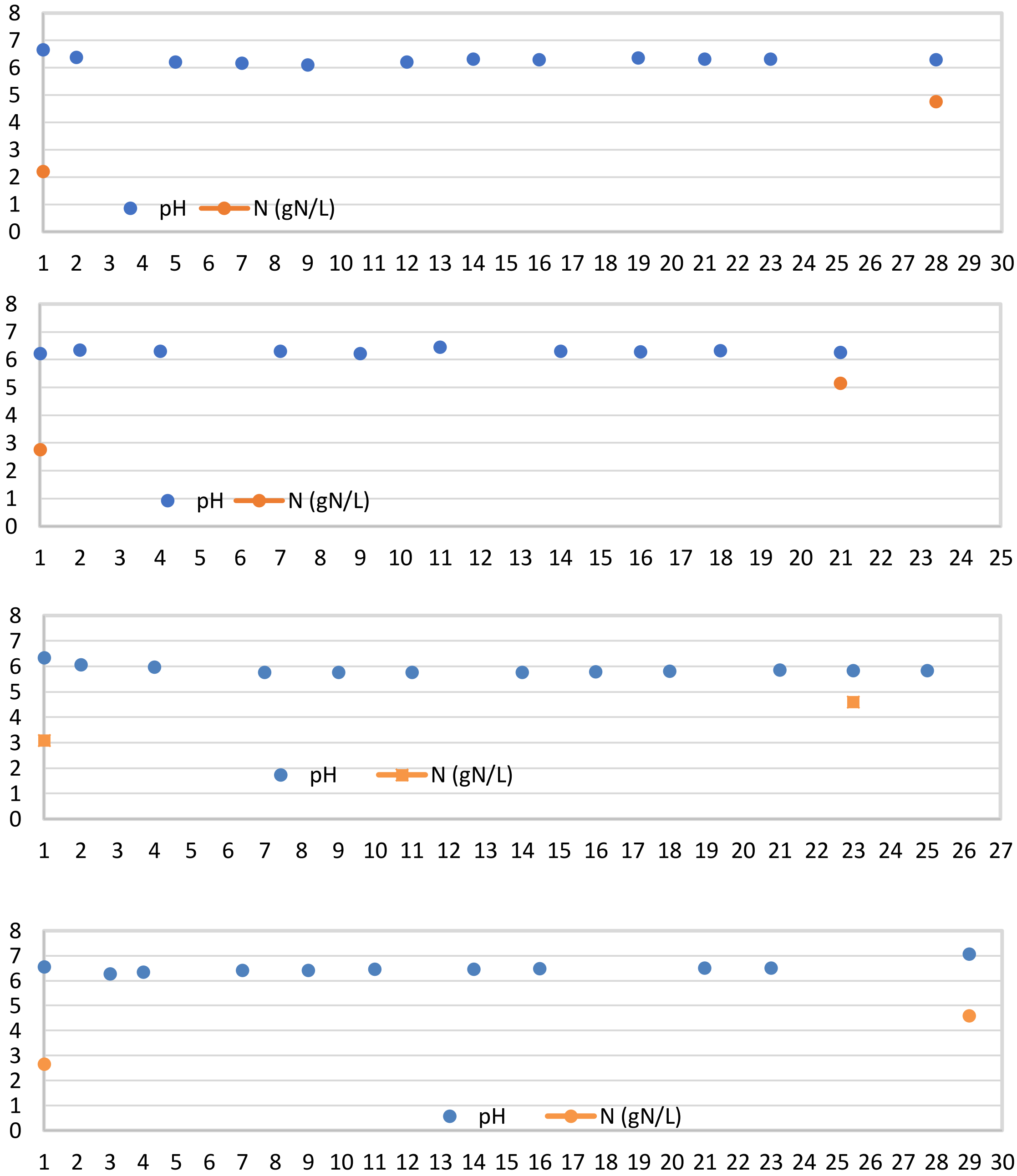

Figure 2A. pH and ammonia monitoring on profiles at 35 ^{o}C: (13/02/2019), (26/02/2019), (19/03/2019) and (30/04/2019), respectively.

ANNEX II: Below is represented the pH and initial/final ammonia concentration monitored on profiles at 20, 45, 55 and 70 ^{o}C, respectively.

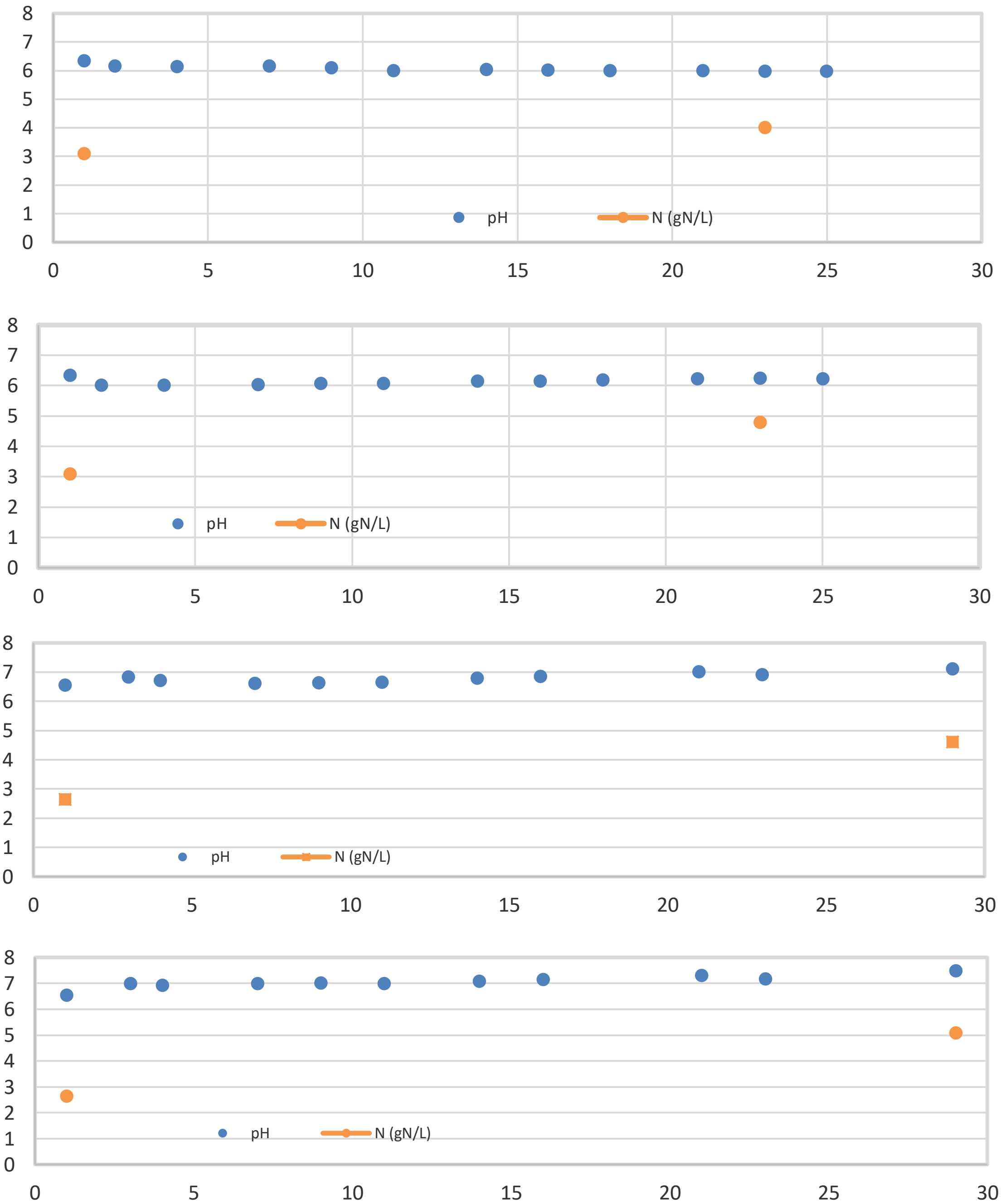

Figure 3A. pH and ammonia monitoring on profiles at 20 ^{o}C (19/03/2019), 45 ^{o}C (19/03/2019), 55 ^{o}C (30/04/2019) and 70 ^{o}C (30/04/2019), respectively.

ANNEX III: On the following plots are shown the different speciation that were find on batch fermentation assays at 35 ^{o}C.

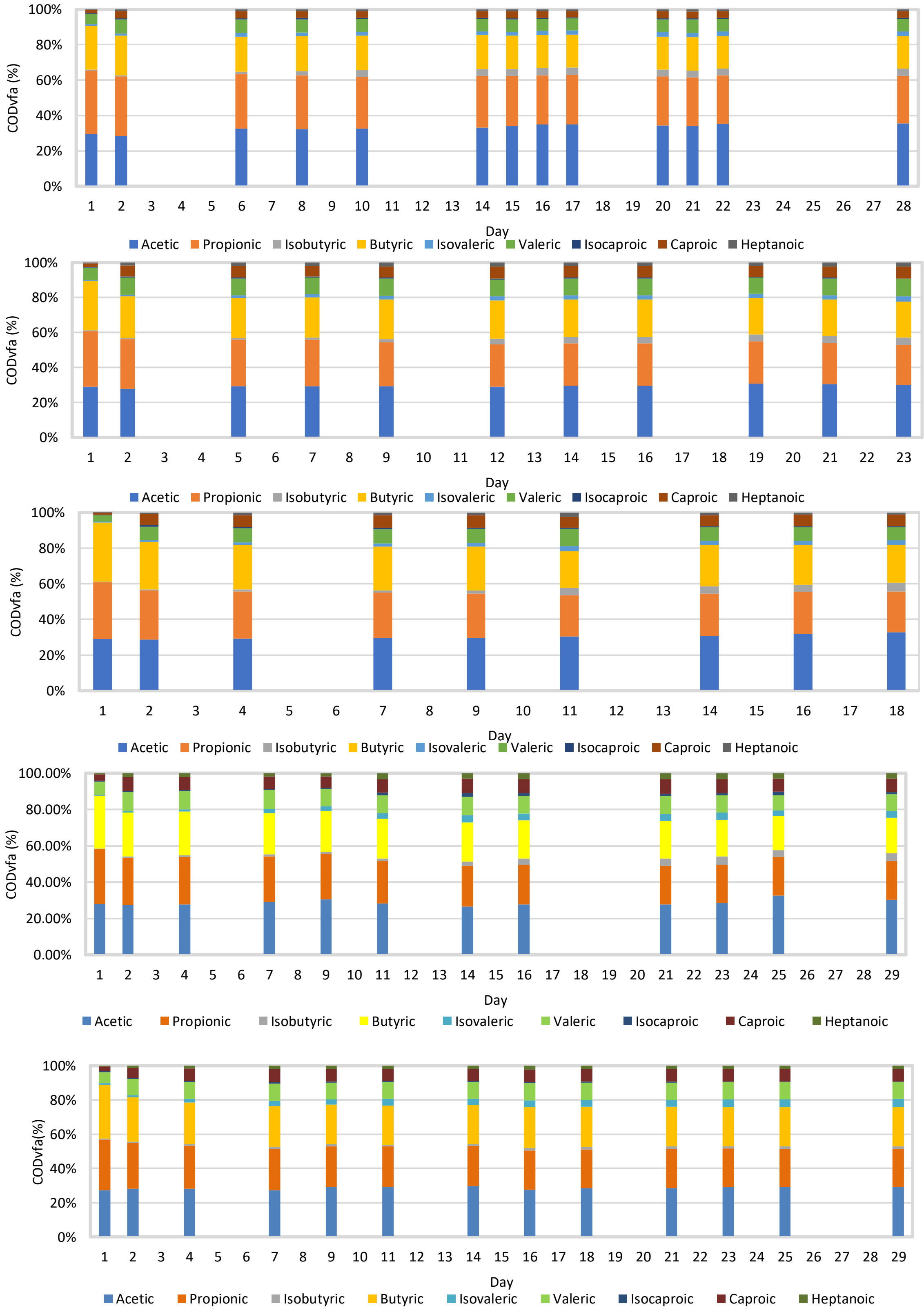

Figure 4A. VFA speciation on Profiles 1,2,3,4 and 5, respectively.

<u>ANNEX IV:</u> On the following plots are shown the different speciation that were find on batch fermentation assays at 20, 45, 55 and 70 ^{o}C .

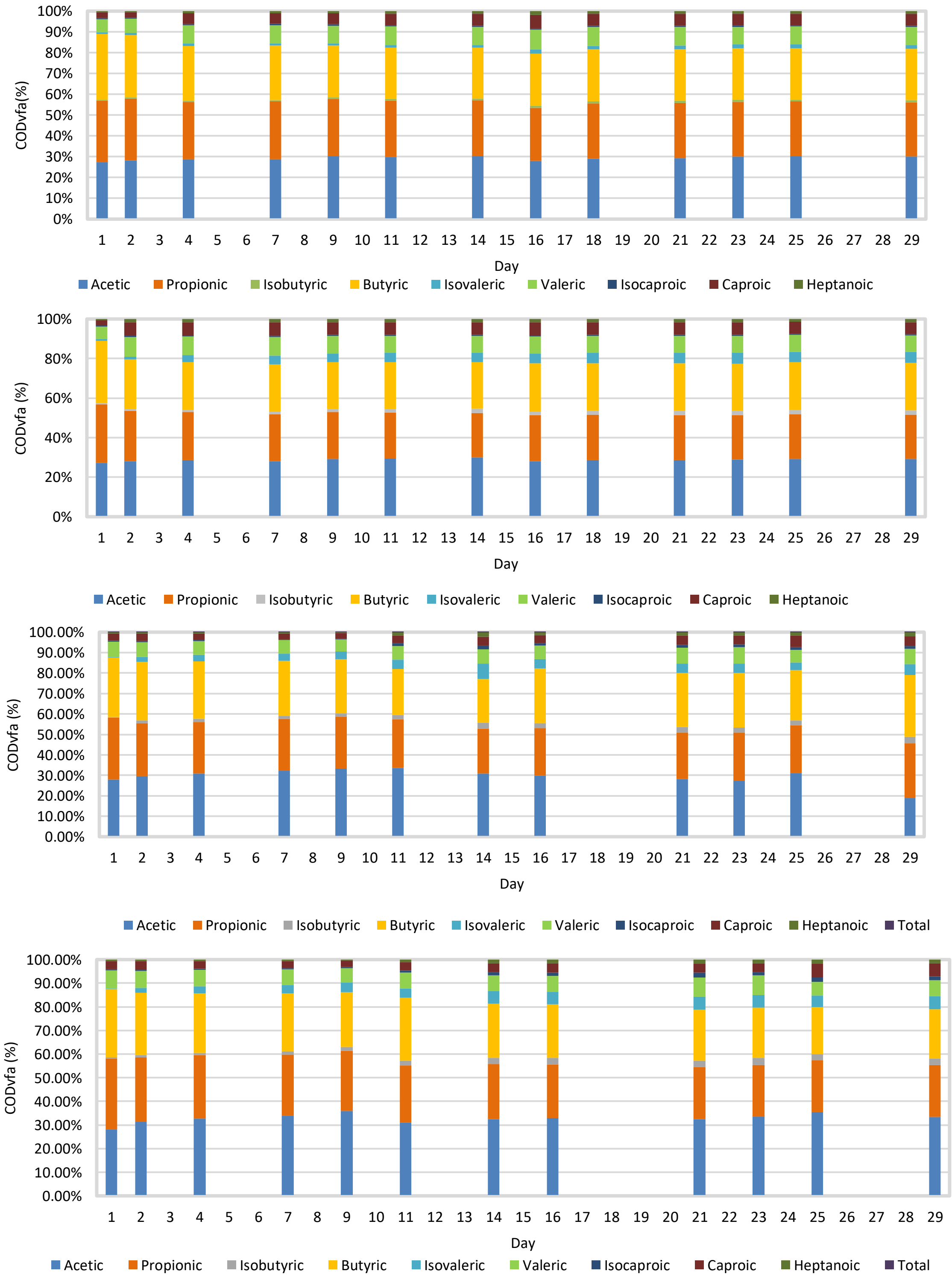

Figure 5A. VFA speciation on Profiles at 20, 45, 55 and 70 ^{o}C, respectively.

Annex V:

Tabla 1A. Gantt chart representation.

TASKS		Cronogram (weeks)																	
Task	Description	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
T01	*Read previous information about the topic*	✓	✓																
T02	*Laboratory set-up*		✓	✓	✓														
T03	*Analysis of MBT streams collected periodically in a biological mechanical treatment plant*					✓	✓	✓	✓	✓	✓		✓	✓					
T04	*Performing fermentation batch assays to evaluate the production and speciation of volatile fatty acids and main parameters.*						✓	✓	✓	✓	✓		✓	✓	✓	✓			
T05	*Assessment of temperature impact on fermentation batch assays.*								✓	✓	✓		✓	✓	✓	✓			
T06	*Data analysis (MBT streams and batch assays)*								✓	✓				✓	✓	✓	✓	✓	
T07	*Writing Master's Thesis*							✓	✓	✓	✓			✓	✓	✓	✓	✓	
T08	*Oral presentations*										✓								✓